FORM PTO-1390 (Modified) (REV 11-98) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: **P 61771 US 0**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR): **09/744932**

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/BE99/00094	**26 JULY 1999**	**31 JULY 1998**

TITLE OF INVENTION

DEEP COLOURED GREEN-TO-BLUE SHADE SODA-LIME GLASS

APPLICANT(S) FOR DO/EO/US

COSTER, Dominique; FOGUENNE, Marc

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ Certificate of Mailing by Express Mail
20. ☒ Other items or information:

Certification of Translation of Application Into English

526 Rec'd PCT/PTO 31 JAN 2001

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
09/744932	PCT/BE99/00094	P 61771 US 0

21. The following fees are submitted:.

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

		CALCULATIONS PTO USE ONLY
☐	Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO	**$1,000.00**
☒	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but Internation Search Report prepared by the EPO or JPO	**$860.00**
☐	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO	**$710.00**
☐	International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4)	**$690.00**
☐	International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)	**$100.00**

ENTER APPROPRIATE BASIC FEE AMOUNT = **$860.00**

Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☒ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)). **$130.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	23 - 20 =	3	x $18.00	**$54.00**
Independent claims	1 - 3 =	0	x $80.00	**$0.00**
Multiple Dependent Claims **(check if applicable)**.			☐	**$0.00**

TOTAL OF ABOVE CALCULATIONS = **$1,044.00**

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) **(check if applicable).** ☐ **$0.00**

SUBTOTAL = **$1,044.00**

Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). + **$0.00**

TOTAL NATIONAL FEE = **$1,044.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).** ☐ **$0.00**

TOTAL FEES ENCLOSED = **$1,044.00**

Amount to be: refunded	$
charged	$

☒ A check in the amount of **$1,044.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. in the amount of to cover the above fees.
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **01-2520** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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Jerold I. Schneider
NAME

24,765
REGISTRATION NUMBER

31 January 2001
DATE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re:

Applicant:	COSTER et al
Application No.:	unknown- filed concurrently
Filing Date:	Filed concurrently
For:	Deep Coloured Green-to-Blue Shade Soda-Lime Glass
Int'l. Application No:	PCT/BE99/00094
Int'l. Filing Date:	26 July 1999

Assistant Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir:

Prior to assigning an Application Number, and prior to any action on the merits, please amend this application as follows:

Page 1, prior to line 1, insert

- - CROSS REFERENCE TO RELATED APPLICATIONS

This application is based upon, and claims priority from International Application No., PCT/BE99/00094 filed 26 July 1999, and French Application No. 98/10020 filed 31 July, 1998, both of which are hereby incorporated by reference.

BACKGROUND OF THE INVENTION - -

Page 1, line 31, change "2" to - - two - - ;

Page 4, after line 12, insert

- - SUMMARY OF THE INVENTION - -

Page 12, after line 4, insert

- - DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS - -

In the claims:

Cancel claims 1-19 and replace them with the following new claims 20 through 42.

-- 20. A colored soda-lime glass composed of glass-forming principal constituents and of coloring agents, characterized in that it contains from 0.40 to 0.52% by weight of FeO and has, under illuminant A and for a glass thickness of 4 mm, a light transmission (TLA4) of less than 70%, a selectivity (SE4) of greater than 1.65 and an ultraviolet radiation transmission (TUV4) of less than 8%.

21. The colored glass in accordance with claim 20, characterized in that it has a selectivity (SE4) of at least 1.70.

22. The colored glass in accordance with claim 20, characterized in that it has a selectivity (SE4) of at least 1.75.

23. The colored glass in accordance with claim 20, characterized in that it has a light transmission greater than 15% and less than 50%.

24. The colored glass in accordance with claim 20, characterized in that it has a light transmission greater than 20% and less than 45%.

25. The colored glass in accordance with claim 20, characterized in that it has, for a glass thickness of 5 mm, a dominant wavelength (λ_D) of less than 550 nm,.

26. The colored glass in accordance with claim 20, characterized in that is has, for a glass thickness of 5 mm, a dominant wavelength (λ_D) of less than 520 nm.

27. The colored glass in accordance with claim 20, characterized in that it has a purity (P) of greater than 9%.

28. The colored glass in accordance with claim 20, characterized in that it has a purity (P) of greater than 10%.

29. The colored glass in accordance with claim 20, characterized in that it contains, in addition to Fe, at least one coloring agent selected from the group consisting of Cr, Co, V, Se, Ti, Ce, Mn.

30. The colored glass in accordance with claim 20, characterized in that it has the following optical properties:

$20\% < TLA4 < 40\%$

$15\% < TE4 < 25\%$

$0\% < TUV4 < 5\%$

$480\ nm < \lambda_D < 520\ nm$

$10\% < P < 20\%$.

31. The colored glass in accordance with claim 20, characterized in that it comprises coloring agents in the following percentages by weight, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	1.2 to 1.85%
FeO	0.40 to 0.50%
Co	0.0020 to 0.0130%
Cr_2O_3	0 to 0.0240%
V_2O_5	0 to 0.1%
Se	0 to 0.0015%.

32. The colored glass in accordance with claim 20, characterized in that it has the following optical properties:

$25\% < TLA4 < 35\%$

$15\% < TE4 < 20\%$

$0\% < TUV4 < 3.5\%$

$495 \text{ nm} < \lambda_D < 500 \text{ nm}$

$10\% < P < 15\%$.

33. The colored glass in accordance with claim 20, characterized in that it has a TLA4 of less than 30%.

34. The colored glass in accordance with claim 20, characterized in that it has a TLA4 of less than 28%.

35. The colored glass in accordance with claim 20, characterized in that it comprises coloring agents in the following percentages by weight, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	1.45 to 1.85%
FeO	0.40 to 0.45%
Co	0.0030 to 0.0120%
Cr_2O_3	0.0190 to 0.0230%
V_2O_5	0.0350 to 0.0550%
Se	0 to 0.0010%.

36. The colored glass in accordance with claim 20, characterized in that its percentage by weight of FeO is greater than 0.42.

37. The colored glass in accordance with claim 20, characterized by the absence of Se as a coloring agent.

38. The colored glass in accordance with claim 20, characterized in that it has, for a thickness of 5 mm, a light transmission under illuminant C (TLC5) of between 15% and 35%.

39. The colored glass in accordance with claim 20, characterized in that it is coated with a layer of at least one metal oxide.

40. The colored glass in accordance with claim 20, characterized in that it is in sheet form.

41. A window for an automobile made in accordance with claim 20.

42. A laminated glazing made in accordance with claim 20. - -

REMARKS

The amendment to the specification is to put the application into U.S. form. New claims are presented prior to any action by the U.S. Patent and Trademark Office.

Respectfully submitted

January 31, 2000

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DEEP COLOURED GREEN-TO-BLUE SHADE SODA-LIME GLASS

The present invention relates to a deep-colored soda-lime glass of green-to-blue shade, composed of glass-forming principal constituents and of coloring agents.

The expression "soda-lime glass" is used here in a wide sense and relates to any glass which contains the following constituents (in percentages by weight):

Na_2O	10 to 20%
CaO	0 to 16%
SiO_2	60 to 75%
K_2O	0 to 10%
MgO	0 to 10%
Al_2O_3	0 to 5%
BaO	0 to 2%
BaO + CaO + MgO	10 to 20%
$K_2O + Na_2O$	10 to 20%.

This type of glass is very widely used in the field of glazing for buildings or automobiles, for example. It is usually manufactured in the form of a ribbon by the drawing or float process. Such a ribbon can be cut into sheets which can then be bent or can undergo a treatment to improve the mechanical properties, for example a thermal toughening step.

When referring to the optical properties of a glass sheet, it is generally necessary to relate these properties to a standard illuminant. In the present description, 2 standard illuminants are used, namely illuminant C and illuminant A defined by the Commission Internationale de l'Eclairage (C.I.E.). Illuminant C represents average daylight having a color temperature of 6700 K. This illuminant is especially useful for evaluating the optical properties of glazing intended for buildings. Illuminant A represents the radiation of a Planck radiator with a temperature of about 2856 K.

This illuminant describes the light emitted by car headlights and is essentially intended to evaluate the optical properties of windows intended for automobiles. The Commission Internationale de l'Eclairage has also published a document entitled "Colorimétrie, Recommandations Officielles de la C.I.E. [*Colorimetry and Official Recommendations of the C.I.E.*]" (May 1970) which describes a theory in which the colorimetric coordinates for light of each wavelength of the visible spectrum are defined so as to be able to be represented on a diagram having orthogonal axes x and y, called the C.I.E. trichromatic diagram. This trichromatic diagram shows the location representative of light of each wavelength (expressed in nanometers) of the visible spectrum. This location is called the "spectrum locus" and light whose coordinates lie on this spectrum locus is said to have 100% excitation purity for the appropriate wavelength. The spectrum locus is closed by a line called the purple boundary which connects the points of the spectrum locus whose coordinates correspond to wavelengths of 380 nm (violet) and 780 nm (red). The area lying between the spectrum locus and the purple boundary is that available for the trichromatic coordinates of any visible light. The coordinates of the light emitted by illuminant C, for example, correspond to x = 0.3101 and y = 0.3162. This point C is regarded as representing white light and consequently has an excitation purity equal to zero for any wavelength. Lines may be drawn from the point C to the spectrum locus at any desired wavelength and any point lying on these lines may be defined not only by its x and y coordinates but also as a function of the wavelength corresponding to the line on which it lies and on its distance from the point C relative to the total length of the wavelength line. Consequently, the color of the light transmitted by a colored glass sheet may be described by its dominant wavelength and its excitation purity expressed as a percentage.

In fact, the C.I.E. coordinates of light transmitted by a colored glass sheet will depend not only on the composition of the glass but also on its thickness. In the present description, and in the claims, all the values of the excitation purity P, of the dominant wavelength λ_D of the transmitted light, and of the light transmission factor of the glass (TLC5) are calculated from the spectral specific internal transmissions (SIT_λ) of a glass sheet 5 mm in thickness. The spectral specific internal transmission of a glass sheet is governed solely by the absorption of the glass and can be expressed by the Beer-Lambert law:

$SIT_\lambda = e^{-E.A_\lambda}$ where A_λ is the absorption coefficient (in cm^{-1}) of the glass at the wavelength in question and E is the thickness (in cm) of the glass. To a first approximation, SIT_λ may also be represented by the formula:

$$(I_{3\lambda} + R_{2\lambda}) / (I_{1\lambda} - R_{1\lambda})$$

where $I_{1\lambda}$ is the intensity of the visible light incident on a first face of the glass sheet, $R_{1\lambda}$ is the intensity of the visible light reflected by this face, $I_{3\lambda}$ is the intensity of the visible light transmitted from the second face of the glass sheet and $R_{2\lambda}$ is the intensity of the visible light reflected by this second face toward the interior of the sheet.

In the description which follows and in the claims, the following are also used:

- for illuminant A, the total light transmission (TLA) measured for a thickness of 4 mm (TLA4). This total transmission is the result of the integration between the 380 and 780 nm wavelengths of the expression: $\Sigma\ T_\lambda.E_\lambda.S_\lambda/\Sigma\ E_\lambda.S_\lambda$ in which T_λ is the transmission at the wavelength λ, E_λ is the spectral distribution of illuminant A and S_λ is the sensitivity of the normal human eye as a function of the wavelength λ;
- the total energy transmission (TE) measured for a thickness of 4 mm (TE4). This total transmission is the result of the integration between the 300 and 2150 nm wavelengths of the expression: $\Sigma T_\lambda.E_\lambda/\Sigma E_\lambda$ in which E_λ is

the spectral energy distribution of the sun at 30° above the horizon;

- the selectivity (SE) measured as the ratio of the total light transmission for illuminant A to the total energy transmission (TLA/TE);

- the total transmission in the ultraviolet, measured for a thickness of 4 mm (TUV4). This total transmission is the result of the integration between 280 and 380 nm of the expression: $\Sigma T_\lambda . U_\lambda / \Sigma U_\lambda$ in which U_λ is the spectral distribution of the ultraviolet radiation that has passed through the atmosphere, defined in the DIN 67507 standard.

The present invention relates in particular to dark-colored glasses of green-to-blue shade. These glasses are generally chosen for their protective properties with respect to solar radiation and their use in buildings is known. They are used in architecture and for partially glazing certain vehicles or railroad compartments.

The present invention relates to a highly selective dark glass of green-to-blue shade which is especially appropriate for use in the make-up of car windows and in particular as rear side windows and as rear window. This is because it is important in the automobile field for the windows of vehicles to provide sufficient light transmission while having as low as possible an energy transmission so as to prevent any overheating of the passenger space in sunny weather. Such glazing may be laminated and may then comprise one or more sheets of glass according to the invention.

The invention provides a colored soda-lime glass composed of glass-forming principal constituents and of coloring agents, which contains from 0.40 to 0.52% by weight of FeO and has, under illuminant A and for a glass thickness of 4 mm, a light transmission (TLA4) of less than 70%, a selectivity (SE4) of greater than 1.65 and an ultraviolet radiation transmission (TUV4) of less than 8%.

The combination of these optical properties is particularly advantageous in that it offers, while ensuring light transmission through the glass sufficient for the uses for which it is intended, a high selectivity value and a low transmission value in the ultraviolet. This makes it possible to avoid both the internal heating of the volumes bounded by windows according to the invention, thereby saving energy when air-conditioning systems are used in said volumes, and the esthetically unattractive discoloration of objects placed inside these volumes, due to the effect of the ultraviolet solar radiation.

Preferably, the glass according to the invention has a selectivity (SE4) of greater than or equal to 1.70, preferably greater than or equal to 1.75. Such selectivity values make it possible to optimize the effectiveness of the thermal filtering of a window for a given light transmission and consequently to improve the comfort within glazed spaces by limiting the extent to which they become overheated when exposed to strong sunlight.

Preferably, the glass according to the invention has a light transmission of greater than 15%, preferably greater than 20%, and less than 50%, preferably less than 45%. These values are well suited to the use of the glass as rear side windows and as rear windows of vehicles.

Advantageously, the dominant wavelength of the glass according to the invention is less than 550 nm, preferably less than 520 nm. Glasses of a shade satisfying these upper limits are regarded as esthetically attractive.

It is preferable that a colored glass according to the invention has a color purity in transmission (P) of greater than 9%, even more preferably greater than 10%. Such purity values give the glass a level of coloration which is appreciated in their specific uses.

Iron is in fact present in most commercially available glasses either as an impurity or introduced

deliberately as a coloring agent. The presence of Fe^{3+} gives the glass a slight absorption of visible light of short wavelength (410 and 440 nm) and a very strong absorption band in the ultraviolet (absorption band centered on 380 nm), whereas the presence of Fe^{2+} ions causes a strong absorption in the infrared (absorption band centered on 1050 nm). The ferric ions give the glass a slight yellow coloration, whereas the ferrous ions give a more pronounced blue-green coloration. All other considerations being equal, it is the Fe^{2+} ions which are responsible for the absorption in the infrared range and which therefore determine the TE. The TE value decreases, thereby increasing the SE value, as the Fe^{2+} concentration increases. By favoring the presence of Fe^{2+} ions over Fe^{3+} ions, a high selectivity is therefore obtained.

Preferably, the glass according to the invention contains, as coloring agent, in addition to iron, at least one of the elements chromium, cobalt, vanadium, selenium, titanium, cerium and manganese. The addition of very small amounts of these elements makes it possible to adjust the optical properties of the glass in an optimum fashion and, especially, to obtain a highly selective glass.

It is possible to produce a glass having roughly a color similar to that of the glass according to the invention using, in particular, nickel as coloring agent. However, the presence of nickel has drawbacks, especially when the glass must be produced by the float process. In the float process, a ribbon of hot glass is conveyed along the surface of a bath of molten tin so that its faces are plane and parallel. In order to prevent oxidation of the tin on the surface of the bath, which would lead to tin oxide being entrained by the ribbon, a reducing atmosphere is maintained above the bath. When the glass contains nickel, this is partially reduced by the atmosphere above the tin bath, giving rise to a haze in the glass produced. This element is also unpropitious to obtaining a high

selectivity value of the glass which contains it, since it does not absorb light in the infrared range, resulting in a high TE value. In addition, nickel present in the glass can form the sulfide NiS. This sulfide exists in various crystalline forms which are stable in different temperature ranges, and the transformations of which, from one form to another, create problems when the glass has to be reinforced by a thermal toughening treatment, as is the case in the automobile field and also in the case of certain glazing products for buildings (balconies, spandrels, etc.). The glass according to the invention, which contains no nickel, is therefore particularly well suited to being manufactured by the float process and to architectural use or in the field of motor vehicles or the like.

The effects of the various coloring agents individually envisioned for producing a glass are the following (according to "Le Verre [*Glass*]" by H. Scholze, translated by J. Le Dû, Institut du Verre [*Glass Institute*], Paris):

- cobalt: the $[Co^{II}O_4]$ group produces an intense blue coloration;

- chromium: the presence of the $[Cr^{III}O_6]$ group gives rise to absorption bands at 650 nm and a light green color. More extensive oxidation gives rise to the $[Cr^{VI}O_4]$ group which creates a very intense absorption band at 365 nm and gives a yellow coloration;

- vanadium: for increasing contents of alkali metal oxides, the color changes from green to colorless, this being caused by the oxidation of the $[V^{III}O_6]$ group into $[V^{V}O_4]$.

- selenium: the Se^{4+} cation has virtually no coloring effect, whereas the uncharged element Se^0 gives a pink coloration. The Se^{2-} anion forms a chromophore with the ferric ions present and consequently gives the glass a red-brown color;

- titanium: the TiO_2 introduced into the glass in a sufficient amount makes it possible to obtain, by

reduction, $[Ti^{III}O_6]$ which colors in the violet or $[Ti^{IV}O_4]$. This coloration may also change to maroon;

- manganese: the $[Mn^{III}O_6]$ group in glasses rich in alkali metals creates a violet color;

- cerium: the presence of cerium ions in the composition makes it possible to obtain a strong absorption in the ultraviolet range. Cerium oxide exists in two forms: $[Ce^{IV}]$ absorbs in the ultraviolet around 240 nm and $[Ce^{III}]$ absorbs in the ultraviolet around 314 nm.

The energy and optical properties of a glass containing several coloring agents are therefore the result of a complex interaction between them. In fact, the behavior of these coloring agents depends greatly on their redox state and therefore on the presence of other elements liable to influence this state.

In preferred embodiments, the glass according to the invention has optical properties which lie within the ranges defined below:

$$20\% < TLA4 < 40\%$$
$$15\% < TE4 < 25\%$$
$$0\% < TUV4 < 5\%$$
$$480\ nm < \lambda_D < 520\ nm$$
$$10\% < P < 20\%.$$

The light transmission range thus defined makes the glass according to the invention particularly useful for reducing the dazzling effect produced by the light from automobile headlights when it is used for the rear side windows or as the rear window of vehicles. The corresponding energy transmission range provides the glass with its high selectivity. As regards the dominant-wavelength and excitation-purity ranges, these correspond to shades and intensity of color which are found to be particularly attractive, especially according to present-day tastes in the architectural and automotive fields.

These properties are obtained from the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	1.2 to 1.85%
FeO	0.40 to 0.50%
Co	0.0020 to 0.0130%
Cr_2O_3	0 to 0.0240%
V_2O_5	0 to 0.1%.
Se	0 to 0.0015%

The use of vanadium as coloring agent has the advantage of limiting the production costs of the glass according to the invention because of the inexpensive nature of this element. Moreover, vanadium is also beneficial in environmental protection terms, due to its low polluting character, and in obtaining the low ultraviolet radiation transmission value of the glass according to the invention. Vanadium also has a high absorption in the infrared radiation range, which helps in obtaining a glass having a low energy transmission and a high selectivity. As regards chromium, its use is not unfavorable to the preservation of the refractory walls of the furnace for manufacturing the glass with respect to which walls chromium poses no risk of corrosion. The use of selenium as coloring agent makes it possible to obtain a more neutral, that is to say more grayish, glass than those not containing this agent.

According to certain especially preferred embodiments, the glass according to the invention has optical properties lying within the following ranges:

$25\% < TLA4 < 35\%$

$15\% < TE4 < 20\%$

$0\% < TUV4 < 3.5\%$

$495\ nm < \lambda_D < 500\ nm$

$10\% < P < 15\%$.

Glass having optical properties lying within the more restricted ranges defined above is particularly efficient since it combines optimal light- and energy-transmission properties for use as rear side windows and rear window of a vehicle. In its architectural use, it combines its esthetic qualities with a considerable energy saving due to less stress on the air-conditioning systems. In the uses in question, it is preferable that the glass according to the invention have a TLA4 of less than 30%, even more preferably less than 28%.

Such properties are obtained from the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	1.45 to 1.85%
FeO	0.40 to 0.45%
Co	0.0030 to 0.0120%
Cr_2O_3	0.0190 to 0.0230%
V_2O_5	0.0350 to 0.0550%
Se	0 to 0.0010%

It is noteworthy that glasses according to the invention containing selenium have a selectivity of greater than or equal to 1.65. Nevertheless, it is preferred for the glass according to the invention not to contain this coloring agent, which is expensive and is incorporated into the glass with a low efficiency.

Preferably, the glass according to the invention has a percentage by weight of FeO of greater than 0.42.

The glass according to the invention is preferably used in the form of sheets having a thickness of 3 or 4 mm for the rear side panes and the rear window of vehicles and thicknesses of more than 4 mm in buildings. When the glass according to the

invention is used in the make-up of laminated glazing, it is preferably used in thicknesses of about 2 mm.

The glass according to the invention also preferably has a total light transmission under illuminant C, for a thickness of 5 mm (TLC5) of between 15 and 35%, which makes it conducive to eliminating the dazzling effect of sunlight when it is used in buildings.

The glass according to the invention may be coated with a layer of metal oxides which reduce its heating by solar radiation and consequently that of the passenger compartment of a vehicle or of a room in a building using such a glass as glazing.

The glasses according to the present invention may be manufactured by conventional processes. In terms of batch materials, it is possible to use natural materials, recycled glass, scoria or a combination of these materials. The colorants are not necessarily added in the form indicated, but this manner of giving the amounts of coloring agents added, in equivalents in the forms indicated, corresponds to standard practice. In practice, the iron is added in the form of red iron oxide or of compounds containing reduced iron (FeO), the cobalt is added in the form of hydrated sulfate, such as $CoSO_4 \cdot 7H_2O$ or $CoSO_4 \cdot 6H_2O$, or of oxides, and the chromium is added in the form of dichromate, such as $K_2Cr_2O_7$. As regards vanadium, this is introduced in the form of sodium oxide or sodium vanadate. The cerium is introduced in the form of oxide or carbonate. The selenium is added in elemental form or in the form of selenite, such as Na_2SeO_3 or $ZnSeO_3$. The titanium is introduced in the form of TiO_2 or of a mixed oxide. As regards the manganese, this is introduced in the form of oxide or salt.

Other elements are sometimes present as impurities in the batch materials used for manufacturing the glass according to the invention, whether in the natural materials, in the recycled glass or in the scoria, but when the presence of these

impurities does not give the glass properties lying outside the limits defined above, these glasses are regarded as being in accordance with the present invention.

The present invention will be illustrated by the following specific examples of optical properties and compositions.

EXAMPLES 1 to 55

Table I gives, by way of nonlimiting indication, the base composition of the glass and the constituents of the glass batch to be melted in order to produce the glasses according to the invention. Tables IIa and IIb give the optical properties and the proportions by weight of the coloring agents of a glass containing or not containing selenium among its coloring agents. These proportions are determined by X-ray fluorescence of the glass and are converted into the molecular species indicated.

The glass mixture may, if necessary, contain a reducing agent, such as coke, graphite or slag, or an oxidizing agent, such as nitrate. In this case, the proportions of the other materials are adapted so that the composition of the glass remains unchanged.

TABLE I

Composition of the base glass		**Constituents of the base glass**	
SiO_2	71.5 to 71.9%	Sand	571.3
Al_2O_3	0.8%	Feldspar	29.6
CaO	8.8%	Lime	35.7
MgO	4.2%	Dolomite	167.7
Na_2O	14.1%	Na_2CO_3	189.4
K_2O	0.1%	Sulfate	5.0
SO_3	0.05 to 0.45%		

TABLE IIa

Ex	Fe_2O_3 (%)	FeO (%)	Co (ppm)	V_2O_5 (ppm)	Cr_2O_3 (ppm)	Se (ppm)	λ_D^* (nm)	P (%)	TLA4 (%)	TE4 (%)	SE4	TUV4 (%)
1	1.80	0.49	31	261	20	2	505.4	9.5	34.0	18.4	1.85	0.9
2	1.70	0.44	61	51	34	3	495.3	12.0	35.1	19.4	1.80	1.2
3	1.81	0.45	58	10	237	9	526.3	8.4	30.3	15.8	1.92	2.0
4	1.67	0.45	75	950	124	5	505.3	8.7	29.9	16.7	1.79	0.6
5	1.71	0.43	81	354	9	3	494.0	12.7	31.8	18.3	1.74	1.2
6	1.58	0.42	67	519	168	14	528.6	7.2	31.4	18.4	1.71	2.1
7	1.68	0.42	78	215	7	12	500.2	7.2	30.7	18.3	1.68	1.7
8	1.42	0.41	78	7	241	8	494.0	13.1	31.9	18.3	1.74	5.0
9	1.55	0.43	82	910	78	3	495.0	13.3	30.0	17.1	1.76	1.5
10	1.47	0.41	69	257	175	9	498.4	9.6	32.6	18.5	1.76	3.7
11	1.63	0.41	75	497	15	12	502.4	6.9	29.5	17.2	1.71	1.4

TABLE IIb

Ex	Fe_2O_3 (%)	FeO (%)	Co (ppm)	V_2O_5 (ppm)	Cr_2O_3 (ppm)	λ_D* (nm)	P (%)	TLA4 (%)	TE4 (%)	SE4	TUV4 (%)
12	1.68	0.46	59	343	197	500.7	11.2	32.8	17.2	1.91	2.2
13	1.62	0.44	60	707	199	501.6	10.8	32.9	17.5	1.88	2.2
14	1.62	0.43	76	469	197	495.9	14.0	31.6	17.4	1.82	2.6
15	1.66	0.43	72	710	100	497.4	12.2	31.8	17.4	1.83	1.9
16	1.59	0.43	100	397	200	491.9	18.2	28.7	16.5	1.74	2.5
17	1.57	0.43	82	465	203	494.4	15.1	31.8	17.8	1.79	2.9
18	1.59	0.42	103	782	193	492.9	17.3	28.0	16.3	1.72	2.2
19	1.63	0.42	74	525	201	497.7	12.7	32.2	17.6	1.83	2.4
20	1.52	0.42	104	399	108	489.3	20.1	30.4	17.9	1.70	3.1
21	1.59	0.42	58	409	197	496.5	13.5	30.8	17.2	1.79	2.2
22	1.59	0.42	63	711	190	502.4	10.3	33.5	18.2	1.84	2.1
23	1.66	0.41	102	623	199	494.3	15.6	28.4	16.6	1.72	1.9
24	1.83	0.50	122	307	137	495.9	14.2	22.1	12.2	1.81	0.5
25	1.71	0.48	60	510	150	499.9	11.6	31.5	15.9	1.98	1.6
26	1.51	0.42	80	462	292	496.5	14.3	31.3	17.4	1.80	3.1
27	1.64	0.42	92	426	295	496.4	14.5	29.2	16.5	1.77	2.2
28	1.57	0.42	72	469	204	496.6	13.1	33.4	18.4	1.81	2.8

Ex	Fe_2O_3 (%)	FeO (%)	Co (ppm)	V_2O_5 (ppm)	Cr_2O_3 (ppm)	λ_D* (nm)	P (%)	TLA4 (%)	TE4 (%)	SE4	TUV4 (%)
29	1.63	0.41	84	497	202	495.9	14.0	31.0	17.4	1.79	2.3
30	1.56	0.40	62	329	204	498.3	11.7	35.5	19.4	1.83	3.0
31	1.51	0.42	80	462	205	494.4	15.3	32.1	17.9	1.80	1.7
32	1.64	0.42	92	426	210	494.2	15.4	29.9	17.0	1.76	1.6
33	1.80	0.47	60	260	6	496.2	12.2	32.8	17.1	1.92	1.8
34	1.78	0.49	82	0	102	492.4	16.9	29.8	15.7	1.90	2.3
35	1.79	0.48	109	516	200	493.9	17.2	25.2	13.8	1.83	1.6
36	1.69	0.49	86	261	206	494.3	16.4	28.4	14.9	1.91	2.3
37	1.68	0.48	103	576	101	490.9	19.8	26.0	14.4	1.81	1.9
38	1.59	0.49	63	431	36	492.8	15.9	32.5	16.9	1.92	2.7
39	1.53	0.47	36	75	213	501	10.9	36.3	18.1	2.01	3.2
40	1.39	0.45	108	750	114	488.2	22.8	30.0	17.3	1.73	4.4
41	1.23	0.48	88	0	109	486.5	25.5	33.8	18.6	1.82	7.7
42	1.22	0.49	61	455	15	487	23.1	36.7	19.6	1.87	7.2
43	1.42	0.44	46	65	238	496.4	13.1	37.4	19.4	1.93	1.9
44	1.77	0.47	96	931	218	498.1	14.0	24.5	13.3	1.84	1.8
45	1.63	0.46	86	178	9	489.7	18.4	32.4	18.2	1.78	1.8
46	1.78	0.48	62	813	236	508.8	9.84	28.9	14.5	1.99	2.0
47	1.58	0.45	95	247	5	488.2	21.2	30.8	17.4	1.77	1.8

Ex	Fe_2O_3 (%)	FeO (%)	Co (ppm)	V_2O_5 (ppm)	Cr_2O_3 (ppm)	λ_D* (nm)	P (%)	TLA4 (%)	TE4 (%)	SE4	TUV4 (%)
48	1.78	0.48	105	878	24	492.1	17.9	24.8	13.8	1.80	1.8
49	1.41	0.48	41	950	15	494.7	12.9	38.2	20.6	1.85	1.9
50	1.42	0.45	79	0	109	490.0	17.7	36.0	20.6	1.75	1.7
51	1.41	0.49	102	852	164	489.1	22.9	28.1	16.1	1.75	1.7
52	1.39	0.48	92	750	54	488.4	21.8	31.6	17.2	1.84	1.8
53	1.70	0.49	59	190	97	495.4	13.5	34.0	17.9	1.90	1.9
54	1.75	0.435	48	0	5	495.4	11.5	38.5	22.0	1.75	1.8
55	1.68	0.43	44	879	35	506.9	8.1	36.8	20.0	1.84	1.8

NB: * = expressed in SI at 5 mm under illuminant C.

CLAIMS

1. A colored soda-lime glass composed of glass-forming principal constituents and of coloring agents, characterized in that it contains from 0.40 to 0.52% by weight of FeO and has, under illuminant A and for a glass thickness of 4 mm, a light transmission (TLA4) of less than 70%, a selectivity (SE4) of greater than 1.65 and an ultraviolet radiation transmission (TUV4) of less than 8%.

2. The colored glass as claimed in claim 1, characterized in that it has a selectivity (SE4) of greater than or equal to 1.70, preferably greater than or equal to 1.75.

3. The colored glass as claimed in either of claims 1 and 2, characterized in that it has a light transmission of greater than 15%, preferably greater than 20%, and less than 50%, preferably less than 45%.

4. The colored glass as claimed in any one of claims 1 to 3, characterized in that it has, for a glass thickness of 5 mm, a dominant wavelength (λ_D) of less than 550 nm, preferably less than 520 nm.

5. The colored glass as claimed in any one of claims 1 to 4, characterized in that it has a purity (P) of greater than 9%, preferably greater than 10%.

6. The colored glass as claimed in any one of claims 1 to 4, characterized in that it contains, in addition to Fe, at least one of the coloring agents Cr, Co, V, Se, Ti, Ce, Mn.

7. The colored glass as claimed in any one of claims 1 to 5, characterized in that it has the following optical properties:

$20\% < TLA4 < 40\%$

$15\% < TE4 < 25\%$

$0\% < TUV4 < 5\%$

$480\ nm < \lambda_D < 520\ nm$

$10\% < P < 20\%$.

8. The colored glass as claimed in claim 7, characterized in that it comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	1.2 to 1.85%
FeO	0.40 to 0.50%
Co	0.0020 to 0.0130%
Cr_2O_3	0 to 0.0240%
V_2O_5	0 to 0.1%
Se	0 to 0.0015%.

9. The colored glass as claimed in any one of claims 1 to 6, characterized in that it has the following optical properties:

$25\% < TLA4 < 35\%$

$15\% < TE4 < 20\%$

$0\% < TUV4 < 3.5\%$

$495\ nm < \lambda_D < 500\ nm$

$10\% < P < 15\%$.

10. The colored glass as claimed in claim 9, characterized in that it has a TLA4 of less than 30%, preferably less than 28%.

11. The colored glass as claimed in claim 9 or 10, characterized in that it comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	1.45 to 1.85%
FeO	0.40 to 0.45%
Co	0.0030 to 0.0120%
Cr_2O_3	0.0190 to 0.0230%
V_2O_5	0.0350 to 0.0550%
Se	0 to 0.0010%.

12. The colored glass as claimed in any one of claims 1 to 11, characterized in that its percentage by weight of FeO is greater than 0.42.

13. The colored glass as claimed in any one of claims 1 to 12, characterized in that it does not contain Se among its coloring agents.

14. The colored glass as claimed in any one of claims 1 to 13, characterized in that it has, for a

thickness of 5 mm, a light transmission under illuminant C (TLC5) of between 15 and 35%.

15. The colored glass as claimed in any one of claims 1 to 14, characterized in that it is coated with a layer of metal oxides.

16. The colored glass as claimed in any one of claims 1 to 15, characterized in that it is in sheet form.

17. The colored glass as claimed in claim 16, characterized in that it is used in the make-up of a window for an automobile.

18. The colored glass as claimed in claim 17, characterized in that it is used in the make-up of laminated glazing.

19. The colored glass as claimed in claim 17 or 18, characterized in that it is used in the make-up of a rear window or rear side window for an automobile.

ABSTRACT

The invention concerns a coloured soda-lime glass deep coloured with a green-to-blue shade. It contains 0.40 to 0.52 wt. % of FeO, present under illuminant A and for a glass thickness of 4mm, a light transmittance (TLA4) less than 70%, a selectivity (SE4) higher than 1.65 and an ultraviolet radiation transmittance (TUV4) less than 8%. Said glass is particularly suited for lateral rear glazing and rear glazing for motor vehicles.

Docket No.
P 61771 US 0

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

DEEP COLOURED GREEN-TO-BLUE SHADE SODA-LIME GLASS

the specification of which

(check one)

☐ is attached hereto.

☒ was filed on **31 January 2001** as United States Application No. or PCT International Application Number **PCT/BE99/00094 and US 09/744932**

and was amended on **31 January 2001 by preliminary amendment**

(If applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)			Priority Not Claimed
PCT/BE99/00094 (Number)	**PCT** (Country)	**26 JULY 1999** (Day/Month/Year Filed)	☐
98/10020 (Number)	**FR** (Country)	**31 JULY 1998** (Day/Month/Year Filed)	☐
(Number)	(Country)	(Day/Month/Year Filed)	☐

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

(Application Serial No.)	(Filing Date)
(Application Serial No.)	(Filing Date)
(Application Serial No.)	(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. *(list name and registration number)*

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